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**EFFECTS OF CONJUGATION IN LENGTH AND  
DIMENSION ON TWO-PHOTON PROPERTIES OF  
FLUORENE-BASED CHROMOPHORES (PREPRINT)**

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## Abstract

We report the computed two-photon (TPA) absorption spectra based upon the results obtained from quadratic response time-dependent density functional theory for fluorene-based donor- $\pi$ -acceptor molecules. Coulomb attenuated functionals with a long-range exchange contribution are applied to predict TPA excitation energies and cross sections and to account for the observed spectral anomalies. The effects of conjugation and multibranching on the TPA spectra are discussed.

## Keywords:

Two-photon

Cross-section

Excitation energies

Excited-state

Diphenylaminofluorene

## 1. Introduction

Large two-photon absorption (TPA) cross-sections of donor-acceptor (DA) chromophores based on the dialkylfluorene core<sup>1-10</sup> make them excellent dyes for potential applications, such as photodynamic therapy,<sup>11</sup> confocal microscopy,<sup>12</sup> fluorescence imaging,<sup>13</sup> and optical memory.<sup>14</sup>

Recently, it has been demonstrated that the design using the multidimensional conjugation DA model significantly increases the observed TPA cross sections.<sup>6,10,15</sup> Using the dipolar system with 2-benzothiazolyl as the  $\pi$ -accepting group (see Figure 1), the conjugation DA model that extends from diphenylamino (AF-240) to triphenylamino (AF-270) groups, can be branched at the amine core to give two quadrupolar (AF-287 and AF-295) and two octupolar (of AF-380 and AF-350) systems.<sup>7,10</sup> A

collection of experimental results for these two series in Table 1 reveals the large effects of conjugation length and dimension on TPA spectral properties. Although we have included single-wavelength TPA measurements for completeness, these TPA cross sections are not sufficient to estimate the enhancement within a series of chromophores due to the differences in spectral shape and location of absorption maxima. However, the spectral locations of these single-wavelength measurements make them useful additions to the full spectra. In addition to the large increase in absorption cross section (Figure 2), the TPA spectra of the octupolar chromophores were found to be totally different from their linear spectra.<sup>10</sup> Thus, these TPA spectra might be governed by different selection rules and transitions<sup>10</sup> that are yet to be assigned.

We have recently<sup>16</sup> carried out a systematic study of the OPA spectra in the gas-phase and in solvents for a variety of AF-X, including the families of chromophores shown in Figure 1, to assess the quality of the ICT excitation energies and absorption intensities calculated by the widely used Becke's three-parameter hybrid functional (B3LYP),<sup>17-19</sup> the hybrid functional of Ernzerhof and Adamo (PBE0)<sup>20,21</sup> and the CAMB3LYP functional of Yanai et al.<sup>22</sup> The CAMB3LYP functional was based on the solution of the Coulomb-attenuated Schrodinger equation for the local density approximation<sup>23</sup> that was extended to apply to generalized gradient approximation based exchange functionals.<sup>24</sup> Thus, CAMB3LYP combines properties of B3LYP and the long-range-correction for the exchange potential by an Ewald split of the  $r_{12}^{-1}$  operator into<sup>22</sup>

$$r_{12}^{-1} = \frac{1 - [\alpha + \beta \cdot \text{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \beta \cdot \text{erf}(\mu r_{12})}{r_{12}}, \quad (1)$$

where  $\alpha$  and  $\beta$  were optimized (for  $\mu = 0.33$ ) with the G2 test set to be 0.19 and 0.46, respectively.

From the computed and experimental results, we were able to gauge the relative accuracy of these functionals. PBE0 excitation energies were found to be in better agreement with experiment than B3LYP, with a mean absolute error (MAE) of 0.16 eV for the first ICT bands, which is similar to a MAE of 0.14 eV obtained for dipolar diphenylaminofluorene-based chromophores.<sup>25</sup> On the other hand, we found that CAMB3LYP overestimates the first ICT band of the nine AF chromophores by an



average of 0.41 eV. At the same time, this overestimation of the excitation energies was alleviated by reducing the amount of the long-range exchange contribution to the total energy with a two-parameter Ewald split of the  $r_{12}^{-1}$  operator as,

$$r_{12}^{-1} = \frac{1 - [\alpha + \alpha \cdot \text{erf}(\mu r_{12})]}{r_{12}} + \frac{\alpha + \alpha \cdot \text{erf}(\mu r_{12})}{r_{12}}, \quad (2)$$

where  $\mu$  and  $\alpha$  are kept unchanged. This modification of CAMB3LYP (*m*CAMB3LYP) was found to have a MAE of 0.07 eV for the first ICT energy of diphenylaminofluorene-based chromophores.<sup>16</sup>

In this study, we focus our attention on the application of the quadratic response time-dependent density functional theory to address outstanding questions concerning the origins and effects of multidimensional conjugation in the observed TPA spectra of these families of chromophores. Theoretically, the TPA spectra of these chromophores are presently uncharacterized, except for AF-240.<sup>25-27</sup>

## 2. Computational Methods

**2.A. Electronic Structure.** The TDDFT calculations were carried out at the previously reported B3LYP/6-31G(d) structures<sup>16</sup> using the same basis set as those used in the ground-state DFT calculations, since the basis set effects were previously<sup>16</sup> found to be small. To gauge the effects of solvent on the TPA cross sections, we applied the nonequilibrium continuum self-consistent reaction field (SCRF) model of Mikkelsen et al.<sup>28</sup> In the SCRF model, the solute is placed in a spherical cavity with the radii ( $a_0$ ) obtained from the largest interatomic distances of the solutes with added adjustments for van der Waals interactions. All electronic structure calculations were carried out using the Dalton program.<sup>29</sup>

**2.B. Two-photon.** The TPA cross section can be obtained by relating the absorption rate<sup>25,30-32</sup> to the TPA transition probability, which was first derived by Goppert-Mayer<sup>33</sup> using second order perturbation theory.<sup>34</sup> Using the normalized Gaussian line shape function,<sup>25,35</sup> the two-photon absorptivity can be written as

$$\delta(2E_\lambda) = \frac{16\pi^4}{c^2 h} \left( \frac{\ln 2}{\pi} \right)^{1/2} E_\lambda^2 \sum_f \frac{|S_{f0}|^2}{E_f^{\text{FWHM}}} \exp \left[ \frac{-4 \ln 2}{(E_f^{\text{FWHM}})^2} (2E_\lambda - E_f)^2 \right], \quad (3)$$

where  $c$  is the speed of light,  $h$  is Planck's constant,  $E_\lambda$  the photon energy,  $S_{f0}$  is the two-photon matrix element for a two-photon transition between the ground- (0) and excited-state  $f$ . In this study, the two-photon matrix elements were computed using the single residue quadratic response<sup>36-38</sup> method for linearly polarized photons with parallel polarization that are averaged over all orientations of the molecule.<sup>39-41</sup> The full-width at half-maximum (FWHM,  $E_f^{\text{FWHM}}$ ) of 0.37 eV, obtained from the experimental TPA spectrum AF-240 in THF,<sup>42</sup> was used in the cross section calculations for AF-240, AF-287, and AF-380. For AF-270, AF-287, and AF-350, a FWHM of 0.44 eV, obtained from the experimental TPA spectrum AF-270 in THF,<sup>10</sup> was used. As previously noted,<sup>25</sup> a TPA cross section computed using a Gaussian lineshape function is a factor 1.48 larger than that obtained with a Lorentzian, and a different definition of degenerate TPA rate leads to the TPA cross-sections twice<sup>26,34,41</sup> that of eq 3.

#### 4. Results and Discussion

The TPA experimental results of maximum energy and cross section are organized in Table 1 while the computed results are tabulated in Table 2. Table 1 also includes single-wavelength TPA measurements, which are useful in some cases where the spectral locations of these measurements were made near the absorption maxima. Table 2 lists the computed excitation energies, cross section for each electronic state, as well as the peak energies and cross sections from the sum of Gaussians that can be directly compared to the corresponding experimental values in Table 1. These experimental values were obtained by digitization of the cited absorption spectra. Overall, we found that qualitative conclusions are not affected by functionals used. For the DA chromophores based on dialkylfluorenes, PBE0 (CAMB3LYP) underestimates (overestimates) the excitation energies while *m*CAMB3LYP predicts more accurate energies (see Supporting Information). Thus, *m*CAMB3LYP results are used for discussion throughout, unless noted otherwise.



## AF-240 and AF-270

The first excited state of AF-240 exhibits strong TPA by simultaneously absorbing two photons, each having half of the excitation energy. Experimentally, TPA maxima of AF-240<sup>42</sup> and its decyl derivative (AF-69)<sup>9,43</sup> are reported to occur at about 3.0-3.2 eV (see Table 1).<sup>9,44</sup> However, the observed peak cross sections vary widely, 72-150 GM. TPA in these dipolar systems have been found to originate from first strongly allowed one-photon states with large changes in dipole moments between the ground and the final state, using the so-called two-state approximation<sup>25,26</sup> and quadratic response methods.<sup>27,45</sup> The computed CAMB3LYP/6-31G(d)//B3LYP/6-31G reported by Rudberg et al.<sup>27</sup> for the first excitation energy (2.58 eV) of AF-240 is about the same as our CAMB3LYP/6-31G(d)//B3LYP/6-31G(d) value. As noted previously, CAMB3LYP overestimates the first excitation energy of AF-240<sup>16</sup> and AF-69<sup>45</sup> by a significant amount, even after accounting for the effects of basis set and solvents. Furthermore, the *m*CAMB3LYP energy of 3.22 eV (3.21 eV in THF) and TPA cross section of 112 GM (120 GM in THF) for AF-69 were found to in better agreement with experiment.<sup>45</sup> Not surprisingly, the effects of solvent on the energy and cross section were also found to be small for AF-240 (see Table 2). The computed AF-240 cross sections are slightly larger due to the smaller FWHM used in the calculations. The predicted cross section of 173 GM is in good agreement with TPF values (cf. Tables 1 and 2).

The dipolar arrangement of AF-270, adding a phenyl ring to AF-240, induces a slight changes in color (0.05 eV blueshift in THF) and intensity (~ 60 GM), as predicted by TDDFT. Comparing the TPF (AF-240) and WC/Z-scan (AF-270) values also indicates a blueshift. However, given the large discrepancies in the TPA cross sections found between the TPF and WC/Z-scan experiments, it is unclear that they can be independently used to study the structure-property relationship. Although the predicted maximum (3.29 eV) is in good agreement with the experimental maximum (3.24 eV), the computed maximum cross section of 219 GM, is much larger than the experimental value of 73 GM.<sup>10</sup>



## AF-287 and AF-295

The TPA spectrum of AF-287 has not been reported. A TPA cross section measurement at 3.10 eV (800 nm) was reported<sup>15</sup> to be 123 GM, 77 GM (a factor of 2.2) larger than the value obtained for AF-240. Interestingly, the corresponding measured cross section for AF-295 of 78 GM is significantly smaller, which resulted in an increase of 42 GM relative to AF-270.<sup>15</sup> The increase in TPA intensity upon going from the dipolar AF-270 to quadrupolar AF-295 is consistent with WC/Z-scan spectra, which show an enhancement (1.8) of about 60 GM at peak intensity. The double branching of AF-270 also produces a slight blue-shift of 0.04 eV for the maximum (see Table 1 and Figure 2). This is smaller than the computed blue-shift of 0.15 eV, which is attributed to the more intense and higher energy of the  $3^1A$  state that largely underlies the first TPA band of AF-295. This band has a shoulder at about 3 eV, which may be assigned to the first ( $2^1A$ ) excited state. The experimental TPA enhancement factor of 1.8 is also smaller than the predicted value of 3.5 for the first band, which is predicted to have a peak cross section of about 750 GM. TDDFT also predicts another peak at 3.81 eV with a slightly larger cross section, which is consistent with the maximum observed at 3.73 eV. The corresponding observed intensity (78 GM), however, is much smaller than the first band and that of the predicted value.

## AF-380 and AF-350

The octupolar designs of AF-380 and AF-350 are based on the triphenylamine core but with three identical branches derived from AF-240 and AF-270, respectively. Experimentally, the TPF spectra of AF-350<sup>42</sup> reveal the first TPA maximum at 3.02 eV with cross sections in the range of 310-455 GM while the second maximum was estimated to occur at  $\geq 3.47$  eV with cross sections in the range of 540-1035 GM. In contrast, the WC/Z-scan spectrum<sup>10</sup> in THF has a progression that appears to peak at 3.24 eV with a cross section of about 208 GM. In addition, two less intense features (Figure 2) at the low and high energy sides that correspond to transition energies of 3.01 eV (121 GM) and 3.38 eV (176 GM) were observed. The first computed transition ( $1^1E$ ) at 3.17 eV with the total predicted cross sections of 306 GM is in reasonable agreement with the TPF results but larger (2.5x) than the WC/Z-scan value.

The next transition ( $2^1A$ ) at 3.47 eV is predicted to have a much larger cross section (1127 GM) which may be assigned to the second band in the TPF spectra.<sup>42</sup>

From the reported<sup>10</sup> WC/Z-scan TPA spectrum in THF, AF-380 is found to have more clearly identified maxima at 1.49 eV (89 GM) and 1.69 eV (223 GM) that correspond to the respective transition energies of 2.98 and 3.38 eV, which may be correlated with the  $1^1E$  (3.02 eV) and  $2^1A$  (3.50 eV) excited states, respectively. The first  $1^1E$  excited state has a total predicted cross section of 258 GM but appears as a shoulder due to a strong overlap with a more intense (1393 GM)  $2^1A$  state. The cross sections of these two transitions are much larger than the WC/Z-scan values. However, given the uncertainty in the computed lineshape, the computed  $1^1E$  cross section is in reasonable agreement with the Z-scan cross section of 157 GM at 3.10 eV,<sup>15</sup> which is a factor of 1.8 larger than the WC/Z-scan value.

## 5. Summary and Conclusions

In summary, the TPA spectra of the dipolar AF-270 and AF-240 are similar but differ markedly from that of their quadrupolar (ie., AF-287, AF-295) and octupolar (ie., AF-350, AF-380) relatives due to the differences in the transitions that underlie their absorption spectra. The order of excitation energies of their first absorption bands is dipolar > quadrupolar > octupolar. The same ordering of TPA color and intensities was experimentally observed. The observed TPA band shifts are attributed to different transitions that underlie the resulting spectra. The first TPA bands in the dipolar systems originate from  $S_1$  while  $S_1$  and  $S_2$  excited states underlie the band in the quadrupolar systems. TDDFT also predicts two transitions ( $1^1E$  and  $2^1A$ ) underlie the lowest energy bands that can be assigned to two absorption peaks that are well-resolved in the two-photon WC/Z-scan (AF-380) and fluorescence spectra (AF-350).

Although theory is generally well correlated with experiment, there are some large deviations in the cross sections. Quantitative comparison with experimental TPA cross sections was found to be complicated by the lineshape functions and the large experimental discrepancies. However, good agreement is observed in some cases. The predicted energies of the two-photon states are in good

agreement with available TPA maxima and account for their spectral anomalies of the quadrupolar and octupolar systems

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**Supporting Information Available:** An expanded version of Table 2 includes results obtained with PBE0 and CAMB3LYP functionals.



Table 1. Experimental TPA cross sections ( $\delta$ , in GM) maxima and corresponding transition energies (in eV).

| Molecule/Solvent          | E(max)      | $\delta$<br>(max) | Method    | Pulse<br>Width | Reference |
|---------------------------|-------------|-------------------|-----------|----------------|-----------|
| <b>AF-240<sup>a</sup></b> |             |                   |           |                |           |
| THF (fluorescein)         | 3.02        | 150               | TPF       | 100 fs         | 42        |
| THF (Coumarin 307)        | 3.06        | 135               | TPF       | 100 fs         | 42        |
| Toluene (fluorescein)     | 3.02        | 140               | TPF       | 100 fs         | 42        |
| Toluene (Coumarin 307)    | 3.06        | 125               | TPF       | 100 fs         | 42        |
| THF (single energy)       | 3.10        | 46                | Z-scan    | 105 fs         | 15        |
| <b>AF-270</b>             |             |                   |           |                |           |
| THF                       | 3.24        | 73                | WC/Z-scan | 140 fs         | 10        |
| THF(single energy)        | 3.14        | 50                | Z-scan    | 140 fs         | 10        |
| THF (single energy)       | 3.10        | 36                | Z-scan    | 105 fs         | 15        |
| <b>AF-287</b>             |             |                   |           |                |           |
| THF (single energy)       | 3.10        | 123               | Z-scan    | 105 fs         | 15        |
| <b>AF-295</b>             |             |                   |           |                |           |
| THF                       | 3.28        | 131               | WC/Z-scan | 140 fs         | 10        |
| THF                       | 3.73        | 78                | WC/Z-scan | 140 fs         | 10        |
| THF(single energy)        | 3.14        | 50                | Z-scan    | 140 fs         | 10        |
| THF (single energy)       | 3.10        | 78                | Z-scan    | 105 fs         | 15        |
| <b>AF-380</b>             |             |                   |           |                |           |
| THF                       | 2.98        | 89                | WC/Z-scan | 140 fs         | 10        |
| THF                       | 3.38        | 223               | WC/Z-scan | 140 fs         | 10        |
| THF(single energy)        | 3.14        | 98                | Z-scan    | 140 fs         | 10        |
| THF (single energy)       | 3.10        | 157               | Z-scan    | 105 fs         | 15        |
| <b>AF-350</b>             |             |                   |           |                |           |
| THF (fluorescein)         | 3.02        | 455               | TPF       | 100 fs         | 42        |
| THF (fluorescein)         | $\geq 3.47$ | 1035              | TPF       | 100 fs         | 42        |

|                        |             |     |           |        |    |
|------------------------|-------------|-----|-----------|--------|----|
| THF (Coumarin 307)     | 3.06        | 430 | TPF       | 100 fs | 42 |
| THF (Coumarin 307)     | $\geq 3.47$ | 655 | TPF       | 100 fs | 42 |
| Toluene (fluorescein)  | 3.02        | 310 | TPF       | 100 fs | 42 |
| Toluene (fluorescein)  | $\geq 3.47$ | 840 | TPF       | 100 fs | 42 |
| Toluene (Coumarin 307) | 3.06        | 310 | TPF       | 100 fs | 42 |
| Toluene (Coumarin 307) | $\geq 3.47$ | 540 | TPF       | 100 fs | 42 |
| THF(single energy)     | 3.12        | 152 | Z-scan    | 135 fs | 7  |
| THF                    | 3.24        | 208 | WC/Z-scan | 140 fs | 10 |
| THF                    | 3.02        | 120 | WC/Z-scan | 140 fs | 10 |
| THF(single energy)     | 3.14        | 133 | Z-scan    | 140 fs | 10 |
| THF (single energy)    | 3.10        | 121 | Z-scan    | 105 fs | 15 |

<sup>a</sup>TPA maxima and cross sections for decyl analog (AF-69): 1) 3.18 eV, 100 GM (Z-scan experiment<sup>9</sup> in THF). 2) 3.22 eV, 72 GM (Fl experiment<sup>44</sup> in hexane). 3) 3.20 eV, 120 GM (WLC experiment<sup>9</sup> in THF).

Table 2. Computed SRQR/6-31G(d) TPA energies (in eV) and cross sections ( $\delta$ , in GM, using Gaussian lineshape). The maximum energies and cross sections obtained from the sum of Gaussian equation are in parentheses.

| Functional/ State       | E             | $\delta^a$  | E             | $\delta^b$  |
|-------------------------|---------------|-------------|---------------|-------------|
| <i>m</i> CAMB3LYP       | <b>AF-240</b> |             | <b>AF-270</b> |             |
| 2 <sup>1</sup> A        | 3.22 (3.24)   | 152 (153)   | 3.29 (3.32)   | 215 (219)   |
| 3 <sup>1</sup> A        | 4.03          | 0           | 3.86          | 272         |
| 4 <sup>1</sup> A        | 4.11 (4.15)   | 291 (331)   | 4.10          | 0           |
| 5 <sup>1</sup> A        | 4.25          | 16          | 4.15 (4.10)   | 415 (530)   |
| 6 <sup>1</sup> A        | 4.35          | 74          | 4.28          | 13          |
| SCRF- <i>m</i> CAMB3LYP |               |             |               |             |
| 2 <sup>1</sup> A        | 3.20 (3.22)   | 172 (173)   | 3.25 (3.29)   | 235 (239)   |
| 3 <sup>1</sup> A        | 4.02          | 0           | 3.84          | 350         |
| 4 <sup>1</sup> A        | 4.09 (4.11)   | 388 (409)   | 4.10          | 1           |
| 5 <sup>1</sup> A        | 4.24          | 19          | 4.14 (4.09)   | 549 (690)   |
| 6 <sup>1</sup> A        | 4.33          | 23          | 4.27          | 15          |
| <i>m</i> CAMB3LYP       | <b>AF-287</b> |             | <b>AF-295</b> |             |
| 2 <sup>1</sup> A        | 3.04          | 61          | 3.17          | 84          |
| 3 <sup>1</sup> A        | 3.35 (3.37)   | 613 (625)   | 3.38 (3.47)   | 629 (756)   |
| 4 <sup>1</sup> A        | 3.94          | 25          | 3.81 (3.81)   | 749 (920)   |
| 5 <sup>1</sup> A        | 3.97 (4.00)   | 812 (949)   | 3.81          | 109         |
| 6 <sup>1</sup> A        | 4.05          | 122         | 4.05          | 6           |
| <i>m</i> CAMB3LYP       | <b>AF-380</b> |             | <b>AF-350</b> |             |
| 1 <sup>1</sup> E        | 3.02          | 129         | 3.17          | 153         |
| 2 <sup>1</sup> A        | 3.50 (3.52)   | 1393 (1422) | 3.46 (3.48)   | 1127 (1316) |
| 2 <sup>1</sup> E        | 3.88          | 11          | 3.78          | 192         |
| 3 <sup>1</sup> A        | 3.94 (3.95)   | 1096 (1136) | 3.78          | 193         |

<sup>a</sup>Using FWHM of 0.37 for AF-240, AF-287, and AF-380.

<sup>b</sup>Using FWHM of 0.44 for AF-240, AF-287, and AF-380.



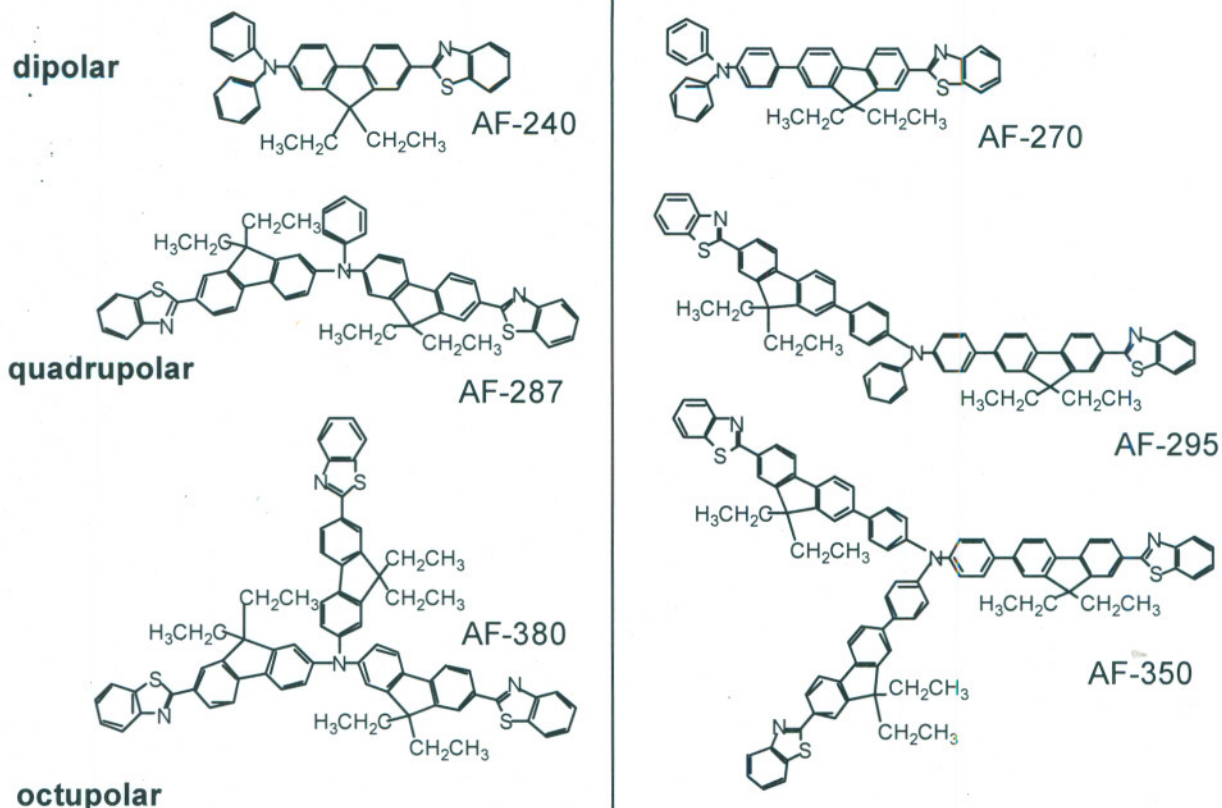


Figure 1: Structures of dipolar, quadrupolar, and octupolar chromophores

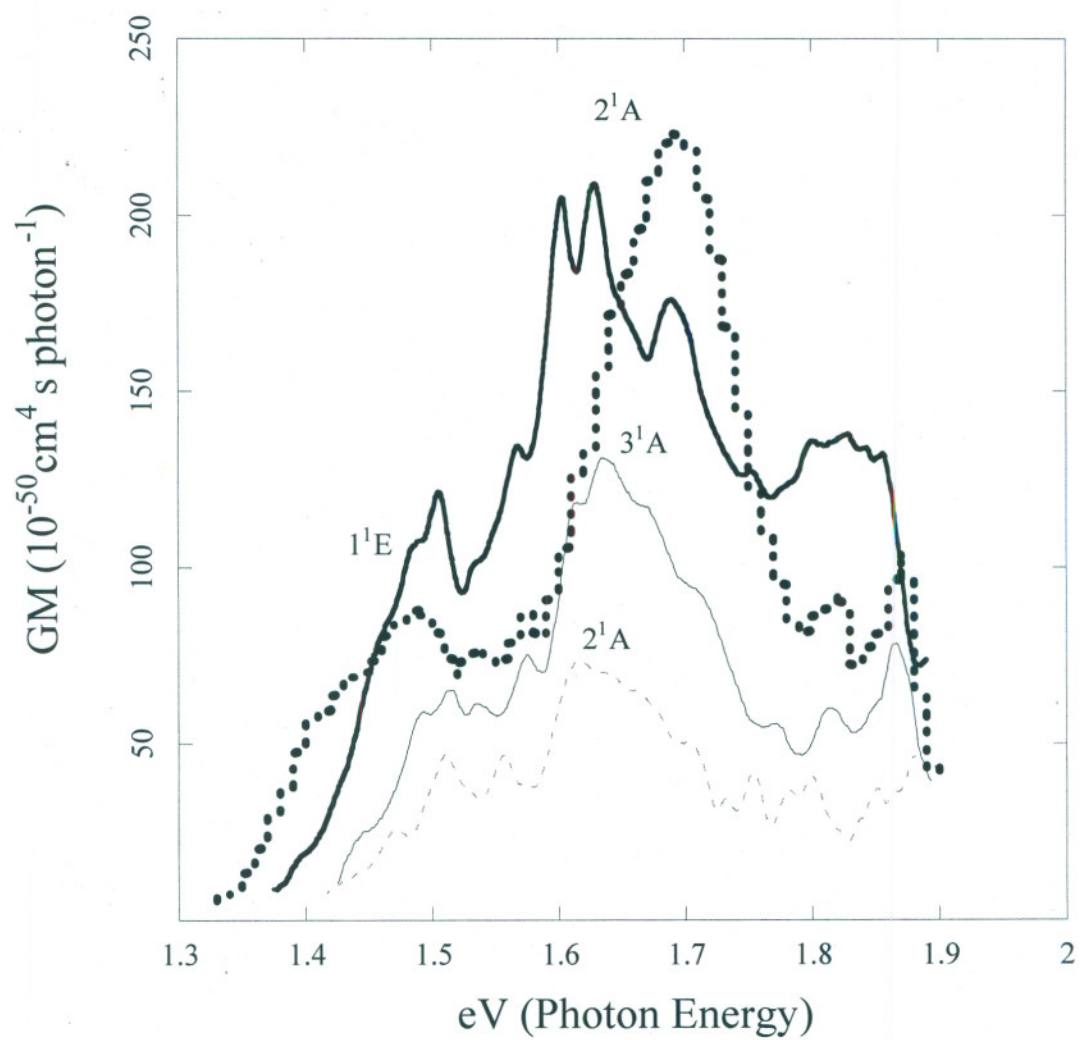


Figure 2: Experimental<sup>10</sup> TPA spectra of AF-270 (dashed), AF-295 (solid), AF-350 (bold) and AF-380 (dashed-bold) in THF.

Table 2S. An expanded version of Table 2. Computed SRQR/6-31G(d) TPA energies (in eV) and cross sections ( $\delta$ , in GM, using Gaussian lineshape). The maximum energies and cross sections obtained from the sum of Gaussian equation are in parentheses.

| Functional/State           | AF-240      |           | AF-270      |           |
|----------------------------|-------------|-----------|-------------|-----------|
|                            | E           | $\delta$  | E           | $\delta$  |
| CAMB3LYP                   |             |           |             |           |
| 2 <sup>1</sup> A           | 3.57 (3.59) | 75 (75)   | 3.66 (3.69) | 64 (65)   |
| 3 <sup>1</sup> A           | 4.35        | 1         | 4.24 (4.27) | 81 (84)   |
| 4 <sup>1</sup> A           | 4.43 (4.47) | 86 (100)  | 4.43        | 0         |
| 5 <sup>1</sup> A           | 4.56        | 12        | 4.58        | 10        |
| 6 <sup>1</sup> A           | 4.66        | 10        | 4.65        | 5         |
| <i>m</i> CAMB3LYP          |             |           |             |           |
| 2 <sup>1</sup> A           | 3.22 (3.24) | 152 (153) | 3.29 (3.32) | 215 (219) |
| 3 <sup>1</sup> A           | 4.03        | 0         | 3.86 (4.10) | 272 (530) |
| 4 <sup>1</sup> A           | 4.11 (4.15) | 291 (331) | 4.10        | 0         |
| 5 <sup>1</sup> A           | 4.25        | 16        | 4.15        | 415       |
| 6 <sup>1</sup> A           | 4.35        | 74        | 4.28        | 13        |
| PBE0                       |             |           |             |           |
| 2 <sup>1</sup> A           | 3.05 (3.07) | 208 (209) | 3.05 (3.08) | 344 (348) |
| 3 <sup>1</sup> A           | 3.90        | 11        | 3.67 (3.77) | 282 (363) |
| 4 <sup>1</sup> A           | 3.96 (4.04) | 433 (560) | 3.94        | 165       |
| 5 <sup>1</sup> A           | 4.14        | 18        | 3.99        | 0         |
| 6 <sup>1</sup> A           | 4.19        | 236       | 4.17        | 15        |
| <sup>a</sup> SCRF-CAMB3LYP |             |           |             |           |
| 2 <sup>1</sup> A           | 3.54 (3.56) | 83 (84)   | 3.62 (3.65) | 70 (71)   |
| 3 <sup>1</sup> A           | 4.35        | 3         | 4.22 (4.25) | 99 (102)  |
| 4 <sup>1</sup> A           | 4.42 (4.44) | 117 (133) | 4.43        | 0         |
| 5 <sup>1</sup> A           | 4.55        | 14        | 4.57        | 11        |
| 6 <sup>1</sup> A           | 4.65        | 8         | 4.64        | 5         |



**Table 2S. Cont.**

<sup>a</sup>SCRF-*m*CAMB3LYP

|                  |             |           |             |           |
|------------------|-------------|-----------|-------------|-----------|
| 2 <sup>1</sup> A | 3.20 (3.22) | 172 (173) | 3.25 (3.29) | 235 (239) |
| 3 <sup>1</sup> A | 4.02        | 0         | 3.84 (4.09) | 350 (690) |
| 4 <sup>1</sup> A | 4.09 (4.11) | 388 (409) | 4.10        | 1         |
| 5 <sup>1</sup> A | 4.24        | 19        | 4.14        | 549       |
| 6 <sup>1</sup> A | 4.33        | 23        | 4.27        | 15        |

<sup>a</sup>SCRF-PBE0

|                  |             |           |             |           |
|------------------|-------------|-----------|-------------|-----------|
| 2 <sup>1</sup> A | 3.02 (3.04) | 238 (239) | 3.02 (3.05) | 386 (390) |
| 3 <sup>1</sup> A | 3.89        | 14        | 3.66 (3.75) | 387 (489) |
| 4 <sup>1</sup> A | 3.94 (4.00) | 567 (693) | 3.93        | 223       |
| 5 <sup>1</sup> A | 4.13        | 22        | 3.98        | 0         |
| 6 <sup>1</sup> A | 4.19        | 288       | 4.16        | 18        |

**AF-287**

**AF-295**

CAMB3LYP

|                  |             |           |             |           |
|------------------|-------------|-----------|-------------|-----------|
| 2 <sup>1</sup> A | 3.41        | 35        | 3.56        | 32        |
| 3 <sup>1</sup> A | 3.74 (3.75) | 221 (226) | 3.76 (3.79) | 121 (147) |
| 4 <sup>1</sup> A | 4.28        | 4         | 4.17        | 31        |
| 5 <sup>1</sup> A | 4.38        | 102       | 4.31 (4.32) | 399 (427) |
| 6 <sup>1</sup> A | 4.41 (4.42) | 373 (478) | 4.38        | 0         |

*m*CAMB3LYP

|                  |             |           |             |           |
|------------------|-------------|-----------|-------------|-----------|
| 2 <sup>1</sup> A | 3.04        | 61        | 3.17        | 84        |
| 3 <sup>1</sup> A | 3.35 (3.37) | 613 (625) | 3.38 (3.47) | 629 (756) |
| 4 <sup>1</sup> A | 3.94        | 25        | 3.81 (3.81) | 749 (920) |
| 5 <sup>1</sup> A | 3.97 (4.00) | 812 (949) | 3.81        | 109       |
| 6 <sup>1</sup> A | 4.05        | 122       | 4.05        | 6         |

PBE0

|                  |      |    |      |     |
|------------------|------|----|------|-----|
| 2 <sup>1</sup> A | 2.86 | 77 | 2.94 | 124 |
|------------------|------|----|------|-----|

**Table 2S. Cont.**

|                   |               |             |               |             |
|-------------------|---------------|-------------|---------------|-------------|
| 3 <sup>1</sup> A  | 3.14 (3.15)   | 863 (885)   | 3.11 (3.13)   | 1017 (1124) |
| 4 <sup>1</sup> A  | 3.78 (3.81)   | 643 (766)   | 3.61 (3.61)   | 414 (571)   |
| 5 <sup>1</sup> A  | 3.80          | 25          | 3.63          | 98          |
| 6 <sup>1</sup> A  | 3.88          | 115         | 3.85          | 60          |
|                   | <b>AF-380</b> |             | <b>AF-350</b> |             |
| CAMB3LYP          |               |             |               |             |
| 1 <sup>1</sup> E  | 3.41 (3.43)   | 68 (138)    | 3.56          | 53          |
| 2 <sup>1</sup> A  | 3.92 (3.94)   | 321 (327)   | 3.83 (4.02)   | 123 (198)   |
| 2 <sup>1</sup> E  | 4.22          | 6           | 4.16          | 76          |
| 3 <sup>1</sup> A  | 4.34          | 140         | 4.16          | 76          |
| <i>m</i> CAMB3LYP |               |             |               |             |
| 1 <sup>1</sup> E  | 3.02          | 129         | 3.17          | 153         |
| 2 <sup>1</sup> A  | 3.50 (3.52)   | 1393 (1422) | 3.46 (3.48)   | 1127 (1316) |
| 2 <sup>1</sup> E  | 3.88          | 11          | 3.78          | 192         |
| 3 <sup>1</sup> A  | 3.94 (3.95)   | 1096 (1136) | 3.78          | 193         |
| PBE0              |               |             |               |             |
| 1 <sup>1</sup> E  | 2.83          | 168         | 2.93          | 230         |
| 2 <sup>1</sup> A  | 3.22 (3.24)   | 1753 (1777) | 3.15 (3.15)   | 1693 (1374) |
| 2 <sup>1</sup> E  | 3.73          | 62          | 3.58          | 213         |
| 3 <sup>1</sup> A  | 3.76 (3.76)   | 387 (456)   | 3.58          | 213         |

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